Reaction of Styrene–Palladium Chloride Complex.—Typically, 1.4 ml (0.01 mol) of triethylamine in 10 ml of benzene was slowly added to a mixture of 2.8 g (0.005 mol) of styrene–palladium chloride complex and 1 g of potassium carbonate in 250 ml of dry benzene. (Potassium carbonate is not always necessary for the reaction, but the filtration of the reaction mixture from palladium metal which deposited on potassium carbonate is much more easy then in the case without it.) The whole was warmed to 70° quickly, and 4 ml (0.156 mol) of methyl alcohol was added. At the same time, carbon monoxide was bubbled into the mixture and the bubbling was continued for 10 min. After cooling, the reaction mixture was filtered and benzene was distilled from the filtrate on a steam bath. Distillation of the condensed mixture under reduced pressure gave 890 mg of the product. Infrared, nmr, and vpc analyses showed that it consisted of methyl cinnamate (0.0041 mol, 41%), dimethyl phenylsuccinate (0.0007 mol, 7%), and methyl hydrocinnamate (0.0003 mol, 3%).

In the case of the ethylene–palladium chloride complex, chloroform was used instead of benzene and the reaction was carried out at 45°.

Registry No.—Styrene–palladium chloride complex, 12313-39-2; triethylamine, 75-50-3; carbon monoxide, 630-08-0.

An Improved Preparation of Specifically Deuterated Methyl Acrylate[1]

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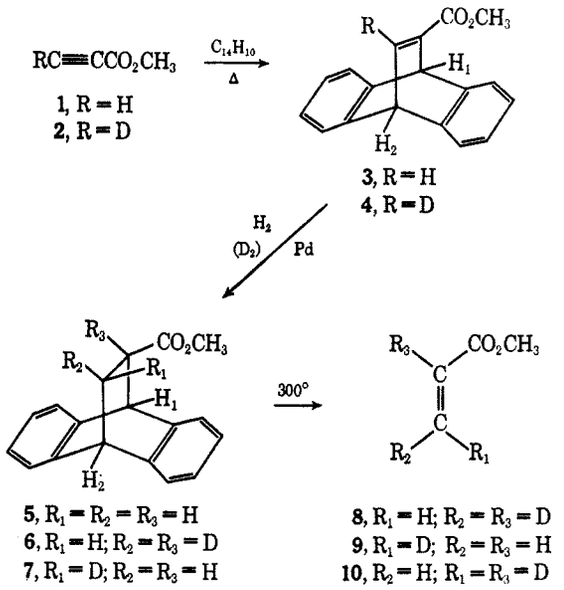
Samples of methyl acrylate stereospecifically deuterated at the β position were required for the preparation of 6α- and 6β-deuterioshikimic acids,[4] necessary for an investigation of the stereochemistry of chorismate formation. A number of β-deuterated acrylates have been prepared recently[5,6] for nmr studies of the conformations of their polymers and bromine adducts. Generally two methods of preparation have been employed: (1) catalytic deuteration of propiolic esters or hydrogenation of deuteriopropiolic esters using the Lindlar catalyst,[5] or (2) homogeneous reduction of propiolic esters with chromous ion in D_2O.[6] A third method, addition of DCl to acetylene followed by conversion to the Grignard reagent and carbonation gave β-deuterioacrylic acid with low (3:2) stereospecificity.[5b]

The chromous ion reduction of acetylenes in D_2O gives exclusive *trans* addition of deuterium,[6,7] but suffers from low yields obtained in reduction of propiolate esters and in the necessity for anhydrous chromous chloride when carrying out reactions in D_2O. We were unable to obtain yields above 10% in reducing methyl propiolate by Schuerch's procedure. Though hydrogenation of acetylenes with the Lindlar catalyst is predominantly *cis*, reduction of propiolate esters has given mixtures of *cis* and *trans* isomers in ratios of 3:1,[5a] 6:1,[5b] and 87:13.[5c] An added difficulty with this method, in our experience, is overreduction to propionates.

We have been able to circumvent both the problems of unsatisfactory stereospecificity and overreduction in the catalytic deuteration of propiolates by the simple expedient of using the anthracene–methyl propiolate Diels–Alder adduct **3**. The increased bulk of the substrate leads to complete stereospecificity in its reduction, while overhydrogenation is impossible. Reduction of **3** with deuterium gas over palladium gave the dideuterio ester **6**, in which the exclusive *cis* configuration of the deuterium atoms was shown by comparison of the nmr spectrum with that of the anthracene–methyl acrylate adduct **5**. The aliphatic protons of **5** are easily differentiated (see Experimental Section); in particular, the hydrogen at R_1 can be distinguished from that at R_2 by the magnitude of the coupling with the hydrogen at R_3 (4 and 12 Hz, respectively). In the spectrum of **6**, the only signal upfield of the methoxy singlet corresponded exactly to the position of R_1, while the clean singlet for H_1 and simple doublet for H_2 further testified to the absence of hydrogens at R_2 and R_3. Pyrolysis of **6** at 290–300° effected retro Diels–Alder dissociation[8] to anthracene and methyl *α-trans-β*-dideuterioacrylate **8**, isolated in 94% yield (Scheme I).

SCHEME I



Comparison of the relative areas of the methyl and olefinic proton signals showed that **8** contained greater than 98% of two deuteriums. The nmr spectrum was identical with that described[5a] for **8**, showing in the olefinic region *only* the 1:1:1 triplet at δ 6.3 due to the β hydrogen *cis* to carbomethoxyl.

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(8) For other examples of retro Diels–Alder reactions, see J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **5**, 211 (1966). The present case provides one of the few clear examples of retention of configuration in the reverse Diels–Alder reaction.

In a similar manner, the adduct **4** of methyl deuteriopropiolate **2** and anthracene was hydrogenated to ester **7**, whose pyrolysis afforded methyl *cis*-β-deuterioacrylate **9**.

Propiolic acid was prepared inexpensively by the decarboxylation[9] of the monopotassium salt of acetylenedicarboxylic acid in water; conducting the decarboxylation in D_2O afforded a simple preparation of deuteriopropiolic acid containing 88% deuterium. The combination of these methods allows a rapid and highly stereospecific preparation of β-deuterated acrylic esters.

Experimental Section

Methyl 3-Deuteriopropiolate (2).—Acetylenedicarboxylic acid monopotassium salt (34 g, 0.224 mol) in deuterium oxide (100 g, 99.8% D_2O) was stirred under nitrogen for 2 hr. The temperature was increased slowly over 6 hr to 100°, and the solution refluxed 1 additional hr. After cooling in an ice bath, the solution was acidified with dilute deuteriosulfuric acid, extracted with five 200-ml portions of ether, dried over magnesium sulfate, concentrated, and distilled *in vacuo* affording 11 g (70%) of 3-deuteriopropiolic acid, bp 45–55° (15 mm).

The 3-deuteriopropiolic acid in methylene chloride (100 ml) and methanol (50 ml) containing a trace of concentrated sulfuric acid was refluxed for 3 days. After being poured into ice water, the organic layer was washed with 10% sodium bicarbonate solution, water, and dried over magnesium sulfate. Removal of the solvent afforded a colorless oil, which was distilled from a spinning-band column giving 10.2 g (77%) of pure methyl 3-deuteriopropiolate, bp 100–101° (740 mm). The ir spectrum (CCl_4) showed strong peaks at 1720 (ester C=O) and 1975 cm^{-1} (–C≡CD). The nmr spectrum (neat) showed peaks at δ 3.41 (s, $-CO_2CH_3$) and 2.90 (s, C≡CH); integration of these peaks showed the presence of 87.5–88.5% of one deuterium.

Methyl Propiolate–Anthracene Adduct (3).—The published procedure[10] for the preparation of the ethyl propiolate adduct was followed. A mixture of anthracene (40 g, 0.225 mol) and methyl propiolate (22 g, 0.262 mol) in anhydrous xylene (100 ml) was refluxed under nitrogen for 7 days. After cooling slowly to room temperature, the crystalline product was filtered and recrystallized from absolute ethanol, affording 39 g (66%) of adduct (**3**), mp 174–175°. Further recrystallization from ethanol raised the melting point to 177–178°: nmr ($DCCl_3$) δ 3.70 (s, 3, $-CO_2CH_3$), 5.20 (d, 1, J = 6 Hz, H_2), 5.68 (d, 1, J = 3 Hz, H_1), 7.85 (dd, 1, J = 6.0 and 3.0 Hz, R = H), and 6.85–7.45 (m, 8, aromatic). Hydrolysis of **3** with alcoholic potassium hydroxide gave in quantitative yield the known acid, mp 248–250° dec (lit.[10] mp 249–250.2° dec).

Methyl 3-Deuteriopropiolate–Anthracene Adduct (4).—Adduct **4** was prepared in the same way from anthracene and methyl 3-deuteriopropiolate (**2**): it melted at 172–174° and showed the parent peak in the mass spectrum at *m/e* 263; nmr ($DCCl_3$) δ 3.70 (s, 3, $-CO_2CH_3$), 5.20 (s, 1, H_2), 5.68 (s, 1, H_1), and 6.85–7.45 (m, 8, aromatic). Comparison of the integrated intensities of the methoxyl and olefinic protons indicated 88% olefinic deuterium.

Catalytic Deuteration of 3.—A solution of adduct **3** (8 g, 30 mmol) in 200 ml of ethyl acetate was stirred with 50 mg of 5% palladium on calcium carbonate under an atmosphere of deuterium (99.9%). The catalyst was filtered after the theoretical consumption of deuterium and the solvent was removed *in vacuo*, affording **6** in quantitative yield, mp 114–115°. Recrystallization from methanol raised the melting point to 117–118° (lit.[11] mp 117–118°): nmr ($DCCl_3$) δ 2.15 (d, 1, J = 5 Hz, R_1 = H), 3.53 (s, 3, $-CO_2CH_3$), 4.66 (s, 1, H_1), 4.30 (d, 1, J = 5 Hz, H_2), and 7.0–7.5 (m, 8, aromatic).

Hydrogenation of Adduct 4.—Ester **7** was prepared in the same manner by catalytic hydrogenation of adduct **4** in 91% yield: mp 114–116°; nmr ($DCCl_3$) δ 3.53 (s, 3, $-CO_2CH_3$), 4.29 (d, 1, J = 5 Hz, H_2), 4.65 (d, 1, J = 5 Hz, H_1), 2.85 (dd, 1, J = 5 and 10.0 Hz, R_3 = H), 1.98 (m, 1, R_2 = H), and 7.0–7.5 (m, 8, aromatic).

Anthracene–Methyl Acrylate Adduct (5).—Adduct **5** was prepared as described by Wawzonek and Hallum[11] and, after recrystallization from methanol, had mp 117–118°; nmr ($DCCl_3$) δ 1.98 (dd, 1, J = 12 and 5 Hz, R_2 = H), 2.10 (dd, 1, J = 5 and 4 Hz, R_1 = H), 2.7–3.0 (m, 1, R_3 = H), 3.53 (s, 3, CO_2CH_3), 4.30 (*t*, 1, J = 5 Hz, H_2), 4.66 (d, 1, J = 5 Hz, H_1), and 7.0–7.5 (m, 8, aromatic).

Methyl α-*trans*-β-Dideuterioacrylate (8).—Ester **6** (8.0 g, 30 mmol) was heated slowly to 290–300° at atmospheric pressure in a simple 25-ml distillation flask equipped with a nitrogen inlet. The volatile ester (bp *ca.* 80°) was slowly released over a 1-hr period and was collected in a receiver cooled to −80°; anthracene sublimed slowly to the neck of the distillation flask and was discarded. The colorless distillate was redistilled, affording 2.4 g (94.5%) of pure **8**: bp 78–80°; nmr (neat) δ 6.3 (1:1:1 t, 1, J = 2.7 Hz, *cis*-β proton) and 3.70 (s, 3, CO_2CH_3). Integrated intensities of these two peaks showed the presence of greater than 98% of two deuteriums in **8**.

Methyl *cis*-β-Deuterioacrylate (9).—Ester **7** (18.0 g, 0.068 mol) was heated to 300° at atmospheric pressure under nitrogen as outlined above, distilling the volatile ester **9** (5.5 g, 93% yield): bp 79–80°; nmr (neat) δ 3.70 (s, 3, CO_2CH_3) and 5.7–6.4 (m, 2.15, olefinic protons). The olefinic region of the nmr spectrum was very similar to the published[5b] spectrum of the corresponding isopropyl ester.

Methyl α-*cis*-β-Dideuterioacrylate (10).—The ester with *trans* deuteriums was prepared by the method used by Schuerch and Fowells[6,12] for the isopropyl ester.

Methyl propiolate (8.5 g, 0.102 mol) was added rapidly to a stirred blue-green solution of chromous chloride (25 g) in deuterium oxide (100 ml, 99.9% D_2O) at 5° under nitrogen. The mixture was stirred at ambient temperature overnight, then saturated with solid ammonium sulfate, extracted with ten 100-ml portions of ether, dried over magnesium sulfate and carefully concentrated. The residual oil was distilled, affording 400 mg (4.5%) of **10**: bp 78–80°; nmr (CCl_4) δ 3.70 (s, 3, $-CO_2CH_3$) and 5.80 (1:1:1 t, 1, J = 1.5 Hz, *trans*-β H). The nmr spectrum was the same in the vinyl region as that reported[6a] for the corresponding isopropyl ester, and showed greater than 98% incorporation of two deuteriums.

Registry No.—**2**, 18910-46-8; **3**, 18910-47-9; **4**, 18910-48-0; **5**, 13294-86-5; **7**, 18916-93-3; **8**, 3321-61-7; **9**, 18910-51-5; **10**, 3321-60-6; 3-deuteriopropiolic acid, 18910-53-7.

(12) We thank Professor Schuerch for his kindness in sending us detailed directions from the Ph.D. thesis of W. Fowells for the chromous chloride reduction.

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Concerning Chlorocarbonium Ions as Intermediates in the Reaction of Ketones with Phosphorus Pentachloride

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In an earlier article,[1] the formation of the products which result from the reaction of ketones with phosphorus pentachloride was explained by assuming that chlorcarbonium ions, R_2ClC^+, were the reactive intermediates. In two later papers,[2,3] arguments that

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